TABLE III

NITRATION OF TOLUENE (50 ML.) WITH RESIN (10 G.) AND A VARIABLE AMOUNT OF NITRIC ACID

90% HNO_3, g.	*ortho–para* ratio
3.0	0.87
3.75	0.92
4.5	0.99
7.5	1.06

TABLE IV

NITRATION OF TOLUENE (250 ML.) WITH A VARIABLE AMOUNT OF RESIN AND NITRIC ACID (2 ML.)

Resin, g.	Yield, g.	*ortho–para* ratio
5	1.52	1.19
20	3.98	0.81
100	4.14	0.68

some temperature dependence. Contrary to the usual pattern of behavior with other nitrating agents, however, the higher *ortho–para* ratios are obtained at the low temperatures, indicating again that this nitrating agent acts in a different manner to those which have been studied before.

A series of nitrations were carried out with 50 ml. of toluene, 15 g. of resin, and 2 ml. of 90% nitric acid. In all cases, the acid was added to a precooled (to 10°) slurry of the resin in toluene. This mixture was then stirred for 1 hr. after which the temperature was raised as rapidly as possible to a given range and maintained there for 1 hr. These reactions were run at nine different temperature ranges, as shown in Table V.

TABLE V

NITRATION OF TOLUENE (50 ML.) WITH RESIN (15 G.) AND 90% NITRIC ACID (2 ML.) AT DIFFERENT TEMPERATURES

Temp., °C.	*ortho–para* ratio	*ortho* ratio
25–30	1.36	No α
35–40	1.36	No α
45–50	1.30	Little α
55–60	1.26	100+
65–70	1.14	50+
75–80	1.06	4.0
85–90	0.98	1.2
95–100	0.90	1.0
105–110	0.90	0.90

Experimental

The ion-exchange resin used in this work was Rohm and Haas Amberlite IR-120. As it is commercially available in the acid form, it normally contains approximately 50% water. If the equivalent weight of the resin is figured at around 200, this would amount to about ten molecules of water per sulfonic acid group, which would be considered a dilute acid. This water can be removed quantitatively by azeotropically refluxing with toluene and removing the water in a Dean–Stark trap. The resin darkens in color and becomes preferentially toluene wetted. It is not immediately wetted by water in its dry state, but on standing reacts exothermically. The dried resin also reacts vigorously with alcohols.

The reactions were run in the usual glass apparatus, equipped for effective stirring, heating, and cooling. Although the resin, when dried, is hygroscopic, no drying tube precautions need be taken when it is slurried in the nonpolar solvent. The dried resin can be weighed in the open air without picking up a detectable amount of water.

The nitrations were carried out by adding 90% nitric acid dropwise to the toluene, or to a mixture of toluene and solvent. When the ion-exchange resin was used, it was mixed with toluene (and solvent) and stirred vigorously as the nitric acid was added. In some cases all the ingredients were mixed and stirred at a low temperature to ensure complete adsorption. Then the temperature was raised rapidly to an arbitrary level and maintained there for a prescribed amount of time.

Reaction samples were taken and treated with solid potassium carbonate. Analysis was made using an Aerograph 600 Hi Fy gas chromatograph which had a 6-ft. column packed with silicone wax on Chromosorb W. *ortho–para* ratios and *ortho–α* ratios were determined using the standard methods. Benzaldehyde, benzyl alcohol, and phenylnitromethane were identified by adding small amounts of authentic samples to the experimental samples.

Halogen Migration in the Reaction of Organic Dihalides with Aluminum Chloride[1]

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This paper comprises the Friedel–Crafts condensation of 1,5-dibromopentane and 1,6-dibromohexane with benzene[1,2] and the isomerization of 1,2-dichlorocyclohexane in the presence of aluminum chloride.

The reaction of 1,5-dibromopentane with benzene was carried out in the presence of a catalytic amount of anhydrous aluminum chloride at room temperature. The 1:1 (dihalide–benzene) condensates and the 1:2 products were separated by fractional distillation. The latter, higher boiling fraction was mainly 1,5-diphenylpentane (19% yield) accompanied by a small amount of isomeric diphenylpentane(s). 1,5-Diphenylpentane was identified by comparison with an authentic specimen.[3]

The lower boiling fraction, which contained 1:1 condensates, was obtained in about 44% yield and gave two peaks on gas–liquid chromatographic (g.l.c.) analysis. Preparative g.l.c. resulted in the isolation of *n*-amylbenzene[4] and 1-methyltetralin[5] in a ratio of 1:1.3, each being identified by comparison with authentic samples.

The reaction of 1,6-dibromohexane was analogously conducted. The 1:2 condensate consisted of 1,6-diphenylhexane[6] (13% yield) and a minor fraction which appeared to be isomeric diphenylhexane(s) (3.8% yield). The lower boiling 1:1 fraction (about 41% yield) was found to show three peaks on g.l.c. in a ratio of 1:14:26. The components were identified

(1) For related work from this laboratory, see (a) K. Sisido and H. Nozaki, *J. Am. Chem. Soc.*, **69**, 961 (1947); (b) K. Sisido and H. Nozaki, *ibid.*, **70**, 1288 (1948); (c) K. Sisido and H. Nozaki, *ibid.*, **70**, 1609 (1948); (d) K. Sisido, Y. Udô, and H. Nozaki, *J. Org. Chem.*, **26**, 1368 (1961); (e) K. Sisido and Y. Yosikawa, *J. Am. Chem. Soc.*, **70**, 1608 (1948).

(2) For the Friedel–Crafts reaction of other organic dihalides, see (a) K. M. Shadmanov, *Dokl. Akad. Nauk. Uz. SSR*, 37 (1957); 40 (1959); 42 (1960); (b) K. M. Shadmanov, *Uzbeksk. Khim. Zh.*, 70 (1961); 57 (1963); (c) W. Reppe, *Ann.*, **596**, 133 (1955); (d) I. P. Tsukervanik, I. M. Kovina, and L. V. Bugrova, *Uzbeksk. Khim. Zh.*, 69 (1958).

(3) N. L. Allinger and D. J. Cram, *J. Am. Chem. Soc.*, **76**, 2364 (1954).

(4) H. Gilman and J. Robinson, "Organic Syntheses," Coll. Vol. II John Wiley and Sons, Inc., New York, N. Y., 1943, p. 47.

(5) R. O. Roblin, Jr., D. Davidson, and M. T. Bogert, *J. Am. Chem. Soc.*, **57**, 151 (1935).

(6) J. Abell and D. J. Cram, *ibid.*, **76**, 4408 (1954).

as *n*-hexylbenzene,[7] 1,4-dimethyltetralin,[8] and 1-ethyltetralin,[9] respectively, by preparative g.l.c. separation and by comparison with authentic samples. Notably the reduction product, *n*-hexylbenzene, was produced in a much lower yield than *n*-amylbenzene in the reaction of 1,5-dibromopentane. This observation was confirmed in duplicate reactions.

When the reaction of 1,6-dibromohexane was conducted at the boiling point of the reaction mixture (80–83°), the yield of *n*-hexylbenzene increased up to 14% and those of 1,4-dimethyltetralin and 1-ethyltetralin were 6.2 and 29%, respectively. At the same time, the yield of 1,6-diphenylhexane decreased to 8%. The formation of isomeric diphenylhexane(s) (8% yield) was clearly observed in this higher temperature reaction, but the structure has not been determined yet. Its infrared spectrum showed a methyl singlet at 1380 cm.$^{-1}$.

Each Friedel–Crafts reaction mentioned above afforded a large quantity of nonvolatile, resinous products which contained no halogen. The possible presence of ω-bromoalkylbenzenes among the products was clearly excluded, and the practical absence of a phenyl group on secondary carbon atoms in the straight-chain alkylbenzenes was established. The source of hydrogen for the production of these reduced species is not clear.

The migration of halogen atoms in carbon chains and rings has often been observed. Nenitzescu and Dinulescu[10] isolated crystalline *trans*-1,4-dibromocyclohexane from the reaction products of *trans*-1,2-dibromocyclohexane with aluminum bromide.[11,12]

In order to gain further information about this problem, *trans*-1,2-dichlorocyclohexane was treated with aluminum chloride in carbon disulfide solution, and the recovered dichlorocyclohexane fraction was analyzed by a g.l.c. method analogous to the one published by Russell, Ito, and Konaka.[13] The dichlorocyclohexane fraction was obtained in about 55% yield and its n.m.r. spectrum indicated the absence of any ring-isomerized compounds. G.l.c. analysis revealed that it contained at least five components as summarized in Table I. Each peak was identified by comparison of the retention time with that of an authentic specimen. The smallest peak at relative retention time of 1.46 could not be characterized owing to its small quantity and to the lack of an authentic sample for comparison, but this peak could reasonably be ascribed to 1,3-dichlorocyclohexane(s) in the light of the work of Russell, *et al.*[13] Thus, the ratio of concentrations of the *cis* and *trans* 1,2 and the *cis* and *trans* 1,4 isomers, represented by the four major peaks on the chromatogram, was found to be approximately 0.5:1:1:1.

TABLE I

G.L.C. ANALYSIS OF THE DICHLOROCYCLOHEXANE ISOMERS PRODUCED FROM *trans*-1,2-DICHLOROCYCLOHEXANE BY THE ACTION OF ALUMINUM CHLORIDE[a]

Relative retention time	Relative compn.[b]	Structure
1[c]	1	*trans*-1,2-
1.25	0.99	*cis*-1,4-
1.33	1.13	*trans*-1,4-
1.46	0.25	. . .
1.93	0.48	*cis*-1,2-

[a] Column: "Polyethylene Glycol 20,000," 4.2 m.; carrier gas: nitrogen at 98 cc./min.; temperature: 132°. [b] As calculated from the peak areas. [c] Actual retention time: 43 min.

Experimental[14]

Reaction of 1,5-Dibromopentane with Benzene.—To a stirred suspension of 12 g. (0.5 mole ratio) of anhydrous aluminum chloride in 140 g. (10 mole ratio) of thiophene-free benzene at room temperature was added 41.6 g. (1 mole ratio) of 1,5-dibromopentane, b.p. 119.5–120.5° (40 mm.), $n^{15}\text{D}$ 1.5132, lit.[15] b.p. 104–106° (19 mm.) (a sample gave a single peak on g.l.c. analysis), over a period of 20 min. and stirring was continued for an additional 15 hr. at this temperature. The reaction mixture was decomposed with acidified ice–water and the organic layer was separated, washed, and dried ($CaCl_2$). Evaporation of benzene followed by distillation under reduced pressure gave two fractions boiling at 58–64° (4 mm.) (11.5 g.) and 139–143° (4 mm.) (12.3 g.), respectively.

A sample (0.8 g.) of the higher boiling fraction was chromatographed on an alumina column and two fractions were obtained. The major fraction (0.5 g.) showed a correct analysis for $C_{17}H_{20}$ and infrared maxima (liquid film) at 3010, 2950, 2870, 1605, 1490, 1030, 740 and 695 cm.$^{-1}$, which were identical with those of an authentic 1,5-diphenylpentane,[3] b.p. 136–139° (2 mm.), $n^{23}\text{D}$ 1.5492. The tetranitro derivative, m.p. 128–129°, was obtained as a yellow solid after recrystallizations from glacial acetic acid and showed a correct analysis for $C_{17}H_{16}N_4O_8$. The minor fraction [0.1 g.; infrared maxima (liquid film): 1380, 884, 825, and 805 cm.$^{-1}$] appears to be isomeric diphenylpentane(s).

G.l.c. analysis of the lower boiling fraction showed two peaks in the ratio of 1:1.3. These were separated by preparative g.l.c. [column: PEG (polyethylene glycol) 20,000; carrier gas: nitrogen, 120 cc./min.; temperature, 170°] and were identified as *n*-amylbenzene and 1-methyltetralin, respectively.

The *n*-amylbenzene fraction showing a correct analysis for $C_{11}H_{16}$ had an infrared spectrum superimposable in every fine detail on that of authentic *n*-amylbenzene; infrared maxima (liquid film): 3070, 2300, 2920, 2860, 1940, 1863, 1800, 1750, 1603, 1499, 1455, 1375, 1030, 906, 741, and 695 cm.$^{-1}$.

The 1-methyltetralin fraction, which showed a correct analysis for $C_{11}H_{14}$, was identified by comparing its infrared spectrum with that of authentic 1-methyltetralin; infrared maxima (liquid film): 3080, 2960, 2900, 1955, 1920, 1810, 1705, 1605, 1590, 1495, 1450, 1378, 1040, 795, 750, and 730 cm.$^{-1}$. The reaction with a smaller amount (0.125 mole ratio) of aluminum chloride gave analogous results.

Reaction of 1,6-Dibromohexane with Benzene.—To a stirred suspension of 1.34 g. (0.125 mole ratio) of anhydrous aluminum chloride in 62.4 g. (10 mole ratio) of benzene at room temperature was added 19.5 g. (1 mole ratio) of 1,6-dibromohexane,[16] b.p. 80° (3 mm.), lit.[17] b.p. 82° (3 mm.), over a period of 10 min. Stirring was continued for an additional 15 hr. at this temperature. Usual work-up of the reaction mixture followed by distillation gave two fractions: b.p. 90–98° (11 mm.), 5.2 g., and b.p. 120–147° (2 mm.), 3.6 g. A portion (1.5 g.) of the higher boiling fraction was purified by chromatography on an alumina column to afford 1.0 g. of pure 1,6-diphenylhexane, $n^{25}\text{D}$ 1.5457,

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(7) I. Simon, *Bull. soc. chim. Belges*, **38**, 53 (1929).

(8) J. Colonge and L. Pichat, *Bull. soc. chim. France*, 855 (1949).

(9) C. M. Staveley and J. C. Smith, *J. Inst. Petrol.*, **42**, 55 (1956).

(10) C. D. Nenitzescu and I. G. Dinulescu, *Acad. rep. populare Romine, Studii cercetari chim.*, **7**, 7 (1959); *Chem. Abstr.*, **53**, 21708 (1959).

(11) H. L. Goering and L. L. Sims [*J. Am. Chem. Soc.*, **79**, 6270 (1957)] observed the formation of *trans*-1,4-dibromocyclohexane *via* 1,1-dibromocyclohexane under the influence of ferric bromide when ionic addition of hydrogen bromide to 1-chlorocyclohexene was conducted. According to their statement, the stereospecificity of the rearrangement excluded the possibility of a free carbonium ion mechanism.

(12) The present authors obtained *trans*-1,4-dibromocyclohexane in 10% yield from the reaction products of *trans*-1,2-dibromocyclohexane with aluminum chloride.

(13) G. A. Russell, A. Ito, and R. Konaka, *J. Am. Chem. Soc.*, **85**, 2988 (1963).

(14) Microanalyses were performed by Miss Kenko Ogawa of this laboratory.

(15) D. W. Andrus, ref. 4, Coll. Vol. III, 1955, p. 692.

(16) Prepared from 1,6-hexanediol according to E. P. Taylor [*J. Chem. Soc.*, 2068 (1958)]. A sample gave a single peak on g.l.c.

(17) P. Baudart, *Bull. soc. chim. France*, [5] **11**, 337 (1944).

showing a correct analysis for $C_{18}H_{22}$. Its infrared spectrum was identical with the authentic sample; infrared maxima (liquid film): 3080, 3050, 2950, 2880, 1615, 1500, 1455, 1032, 905, 746, and 697 cm.$^{-1}$. A minor fraction, n^{24}D 1.5453 (0.3 g.), appeared to be isomeric diphenylhexane(s); infrared maxima (liquid film): 1380 cm.$^{-1}$.

G.l.c. (PEG 20,000) analysis of the lower boiling fraction gave three peaks in the ratio of 1:14:26. The components were separated by preparative g.l.c. (PEG 20,000, 200°; N_2, 120 cc./min.) and were identified as described below to be *n*-hexylbenzene, 1,4-dimethyltetralin, and 1-ethyltetralin, respectively.

When the reaction was conducted at 80–83° for 6 hr., distillation of the reaction products gave two fractions: b.p. 111–112° (26 mm.), 6.6 g., and b.p. 135–148° (1.5 mm.), 3.1 g.

A sample (1 g.) of the higher boiling fraction was purified by chromatography on an alumina column to afford 0.5 g. of pure 1,6-diphenylhexane, n^{25}D 1.5437, which showed a correct analysis for $C_{18}H_{22}$, and 0.5 g. of isomeric diphenylhexane(s), n^{25}D 1.5446; infrared maxima absorption (liquid film): 1380 cm.$^{-1}$.

G.l.c. of the lower boiling fraction gave three peaks: *n*-hexylbenzene, 1,4-dimethyltetralin, and 1-ethyltetralin in the ratio of 14:6.2:29.

The *n*-hexylbenzene fraction showing a correct analysis for $C_{12}H_{18}$ had an infrared spectrum which was identical with that of authentic sample[7]; infrared maxima (liquid film): 2970, 2880, 2810, 1610, 1500, 1450, 1380, 1030, 745, 725, and 700 cm.$^{-1}$.

The 1,4-dimethyltetralin fraction showed a correct analysis for $C_{12}H_{16}$ had an infrared spectrum which was identical with that of authentic 1,4-dimethyltetralin[8]; infrared maxima (liquid film): 3130, 3060, 2990, 2910, 1960, 1930, 1850, 1815, 1715, 1615, 1590, 1500, 1470, 1450, 1380, 1330, 1025, 780, and 750 cm.$^{-1}$. Dehydrogenation of this fraction (0.1 g.) by heating with 0.04 g. of sulfur at 230–240° for 2 hr. gave 1,4-dimethylnaphthalene which was identified in its picrate form, m.p. 142° (lit.[8] m.p. 143°), showing a correct analysis for $C_{18}H_{15}N_3O_7$.

The 1-ethyltetralin fraction also showing a correct analysis for $C_{12}H_{16}$ had an infrared spectrum which was identical with the one of authentic 1-ethyltetralin[9]; infrared maxima (liquid film): 3130, 3070, 2990, 2910, 1960, 1930, 1850, 1810, 1610, 1590, 1500, 1460, 1380, 750, and 730 cm.$^{-.1}$

***trans*-1,2-Dichlorocyclohexane**, b.p. 80–82° (25 mm.), $n^{21.5}$D 1.4898, was prepared by the method of Kharasch and Brown[18] from cyclohexene and sulfuryl chloride and its *trans* configuration was established by comparison of infrared data with published ones.[19] This preparation gave a single peak on g.l.c.

***cis*-1,2-Dichlorocyclohexane.**—The reaction of 2-chlorocyclohexanol[20] with thionyl chloride in the presence of pyridine according to the method of Stevens and Grummit[21] gave a mixture of *cis*- and *trans*-1,2-dichlorocyclohexanes (g.l.c. showed two peaks in the ratio of 3:1), from which pure *cis* isomer was obtained by repeated fractionation, b.p. 89–92° (17 mm.), $n^{20.5}$D 1.4960. This sample gave a single peak on g.l.c., the retention time being 1.93 relative to *trans*-1,2-dichlorocyclohexane.

***cis*- and *trans*-1,4-Dichlorocyclohexanes.**—This mixture, b.p. 72–80° (12 mm.), was prepared by the method of Kwestroo, Meijer, and Havinga,[22] and g.l.c. showed two major peaks with retention times of 1.25 and 1.33 relative to *trans*-1,2-dichlorocyclohexane. Upon cooling, the crystalline *trans*-1,4-dichlorocyclohexane, m.p. 102° (lit.[13] m.p. 102–102.8°), was obtained and its relative retention time on g.l.c. was observed as 1.33.

Izomerization of *trans*-1,2-Dichlorocyclohexane.—A mixture of 50 g. of *trans*-1,2-dichlorocyclohexane, 8.9 g. of aluminum chloride, and 150 ml. of carbon disulfide was stirred at room temperature for 10 hr. The dark reaction product was decomposed with ice–water and acidified with hydrochloric acid; the solvent was removed by steam distillation. The residue was taken up in benzene and the benzene layer was washed and dried ($CaCl_2$). Evaporation of benzene followed by distillation *in vacuo* gave a colorless oil, b.p. 58–60° (9 mm.), n^{21}D 1.4907, which weighed 28.2 g. and showed a correct analysis for $C_6H_{10}Cl_2$.

The g.l.c. data are given in Table I and the n.m.r. spectrum (recorded on Varian-A60 in carbon tetrachloride solution using tetramethylsilane as an internal reference) had two multiplets whose chemical shifts were 1.5–2.5 and 3.8–4.5 p.p.m., respectively. No methyl signal was observed.

In another run, the corresponding fraction (26.4 g.), b.p. 60–77° (12 mm.), was redistilled and the lowest boiling fraction, b.p. 65–69° (11 mm.), was cooled at −35° in a solution of 50 ml. of *n*-pentane. Thus *ca.* 1 g. of colorless crystals melting at 102–102.5° after recrystallization from ethanol was obtained. Mixture melting point with authentic *trans*-1,4-dichlorocyclohexane showed no depression and the infrared spectra were superimposable.

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[18] M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 3432 (1939).

[19] P. Laeboe, J. J. Lothe, and K. Lunde, *Acta Chem. Scand.*, **11**, 1677 (1957).

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A Novel Telomerization Process

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Reaction of oxalyl chloride with olefins is reported to occur only in the case of certain di- and trisubstituted ethylenes.[1,2] These particular reactions result in replacement of an ethylenic hydrogen with the chloroformyl group and apparently occur by an ionic mechanism. Although oxalyl chloride undergoes homolytic decomposition under relatively mild conditions,[3] there are no reports of a free-radical addition to the carbon–carbon double bond.

A Co^{60}-catalyzed reaction between ethylene and oxalyl chloride was discovered in these laboratories during the course of a general investigation of radiation promoted telomerizations. In the first of several preliminary experiments, an equimolar mixture of oxalyl chloride and ethylene (500 p.s.i.) was irradiated 41 hr. at 10^5 rep/hr. and 25°. Analysis (g.l.p.c.) indicated two major products: the 1:1 ($G = 20$) and 2:1 ($G = 70$) telomers $Cl(C_2H_4)_nCOCl$; other products including the 3:1 telomer were formed, but these totaled less than 1% of the combined 1:1 and 2:1 telomer yields. Surprisingly, and in contrast to the broad distribution of products predicted for a "normal" telomerization,[4] the 2:1 telomer was the sole major product at low (*e.g.*, <1:20) oxalyl chloride–ethylene mole ratios. No measurable "dark" reaction was observed and the catalytic effect of radiation was completely nullified by small amounts (*e.g.*, 1%) of molecular oxygen.

These results indicate a short-chain free-radical process in which the 2:1 radical intermediate is subject to an abnormally high incidence of chain transfer. If the chain carrier is assumed to be the chloroxalyl radical, ·COCOCl, then the principal features of the process can be explained by the following sequence of reactions. One addition step (1) followed by chain transfer (2) leads to a nonisolable α-keto acid chloride,

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[1] M. S. Kharasch, S. S. Kane, and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 333 (1942).

[2] F. Bergmann, *et al.*, *ibid.*, **70**, 1612 (1948).

[3] (a) M. S. Kharasch and H. C. Brown, *ibid.*, **64**, 329 (1942); (b) F. Runge, *Z. Elektrochem.*, **56**, 779 (1952); (c) M. T. Ahmed and A. J. Swallow, *J. Chem. Soc.*, 3918 (1963).

[4] See C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 6.